

Hexamethylene diisocyanate as an electrolyte additive for high-energy density lithium ion batteries†

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Hexamethylene diisocyanate can chemically react with the onium ion produced by the oxidation of propylene carbonate and *in situ* generate a novel interfacial layer that is stable at high potential. With an appropriate thickness of this film, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ presents significantly improved rate and cycle performances when tested between 2.5 and 4.6 V (vs. Li/Li^+).

Lithium ion batteries (LIBs) have been rapidly developed since their first commercialization in the 1990s by Sony.¹ To date, this technology has dominated the market of commercial electronic devices and penetrated into the fields of transportation and smart grids.² In contrast to aqueous systems,³ LIB electrolytes utilize liquid carbonates as solvents, which enable their operating window to be widened to 1.2–4.3 V(vs. Li/Li^+).⁴ Although the anodic working potential was pushed to ~ 0.02 V(vs. Li/Li^+) by building a solid electrolyte interphase (SEI) layer,⁵ the progress to lift cathode limitation almost remained static for most of the solid remnants started to decompose above 4.35 V(vs. Li/Li^+).⁴ On the other hand, positively widening the working window could provide the possibility to fully utilize the commercial cathodes such as LiCoO_2 and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$, and enable the evaluation of novel materials including $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMnO}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁶ Obviously, using high-potential electrolytes has become one of the most promising strategies to enhance the cell's energy density.

The utilization of anti-oxidative solvents seems to be the most easily implemented solution. The solvents with strong electron-withdrawing groups, such as sulfone and nitrile,⁷ could endure the oxidation at high potential. Although they exhibited good stability even up to 6 V(vs. Li/Li^+), the electrolytes based on these solvents are not applicable in current commercial systems due to their inability to construct an effective SEI layer on the graphite anode.⁸ Currently, these solvents are utilized as co-

solvents, by which the cut-off potential could be lifted by 100–200 mV. This improvement could be attributed to the absorption of anti-oxidative solvents on the active sites of cathodes.^{7b,9}

Passivating the cathode with an inert layer is an alternative strategy to improve its cyclic stability. Coating inorganic ceramics, such as metal oxides and phosphates, could alleviate the side reactions between the electrolyte solvents and cathodes to make LiCoO_2 work normally at 4.4 V(vs. Li/Li^+) in state-of-the-art electrolytes.¹⁰ Building an organic film with lower HOMO levels is also a feasible strategy, such as the fluorinated decomposed products of phosphides. The fluorine-containing fragments and subsequently generated oligomers present a better stability at high potential, as shown by Choi and Xu *et al.*¹¹ Using a polymer layer is another effective way to ameliorate the cyclic stability. With the appropriate concentration, aromatic derivatives¹² could form a thin layer on the cathode, instead of dimensional growth that will lead to electrical shorting in the cell. However, the following reaction at ~ 4.55 V(vs. Li/Li^+) restricts its further application at higher potential.¹³

In recent efforts, we found that the hexamethylene diisocyanate (HDI) exhibits an interesting film-forming behavior. HDI is a commercially available product, and has been utilized in various fields such as the chemical industry, agriculture and medicine.¹⁴ It also has been investigated as an electrolyte additive for SEI film formation at the anode.¹⁵ However, to the best of our knowledge, the promising performance of HDI as a cathode film-forming additive has not been proposed in the literature. Hence, we will introduce the reaction pathway of film formation and its influence on the electrochemical performance after adding HDI as an additive in this work.

The surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ charged at 4.6 V(vs. Li/Li^+) for 3 h in the investigated electrolytes is first analyzed with TEM. No obvious precipitate is observed in the electrolyte of 1 M LiPF_6 dissolved in PC + DMC(1 : 1, v/v) as shown in Fig. 1a. In the electrolyte with 1 mM HDI, the particle surface almost maintains the same smoothness as the pristine (Fig. 1b). When the HDI concentration increases to 100 mM, some new matter is

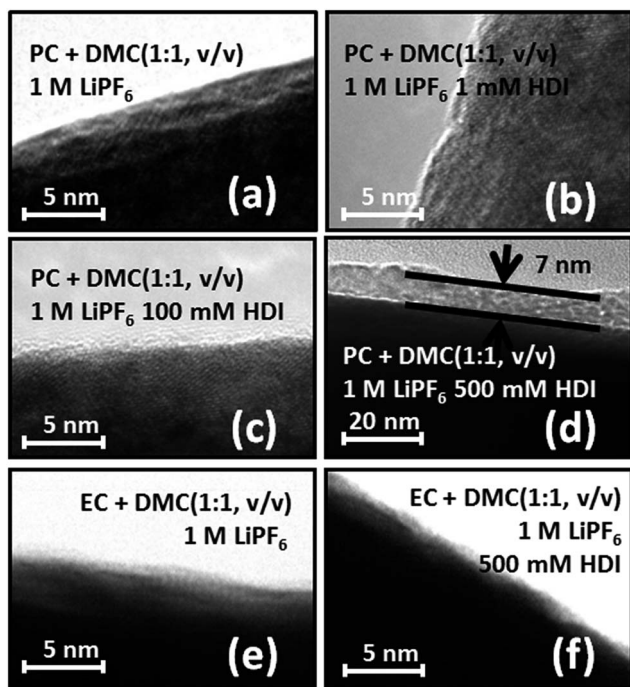


Fig. 1 TEM images of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrodes charged at 4.6 V(vs. Li/Li^+) for 3 h in PC based electrolytes (a) reference electrolyte, (b) with 1 mM HDI added, (c) with 100 mM HDI added, (d) with 500 mM HDI added and EC based electrolytes (e) 1 mol L^{-1} LiPF_6 in EC + DMC (1 : 1, v/v), (f) with 500 mM HDI added.

observed on the cathode (Fig. 1c), and it accumulates to an ~ 7 nm-thick layer in the electrolyte with 500 mM HDI (Fig. 1d). This physical-existence evidence proves that the surface layer generated from HDI is stable at high potential. If it is uniformly deposited on the cathode surface, this layer should be ~ 1.4 nm thick for the electrolyte with 100 mM HDI, and ~ 0.14 Å thick for the system containing 1 mM HDI. As for EC based electrolytes (Fig. 1e and f), no obvious additional layer is identified even in the electrolyte with 500 mM HDI. Since HDI is proved to be stable even at 5 V(vs. Li/Li^+)¹⁶ and as shown in Fig. S4,[†] this characteristic of solvent dependence probably indicates that this layer should have been grown *via* a chemical reaction involving the decomposed species of PC.

To explore the probable reaction pathway, XPS and FTIR are used to analyze the N-based functional group in the generated surface layer (Fig. 2). A new peak related to nitrogen is detected at 401 eV, instead of the isocyanate group from pure HDI (399.7 eV). The higher electron binding energy suggests the reduced outer electron density of N atoms, which could be attributed to the formation of the amide group.¹⁷ From FTIR spectroscopy, two new peaks are identified at 1526 cm^{-1} and 1751 cm^{-1} , corresponding to the vibrations of N-H and C=O of an amide group. Both results indicate that isocyanate groups should have been changed to the amide group during polymerization.¹⁸ Additionally, no signal related to nitrogen is detected on the electrode charged in the electrolyte of EC + DMC with HDI.

According to the obtained results and knowledge on organic chemistry, the *in situ* generated film should be polymerized

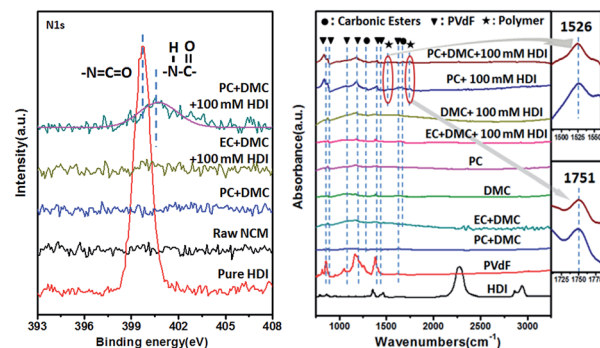
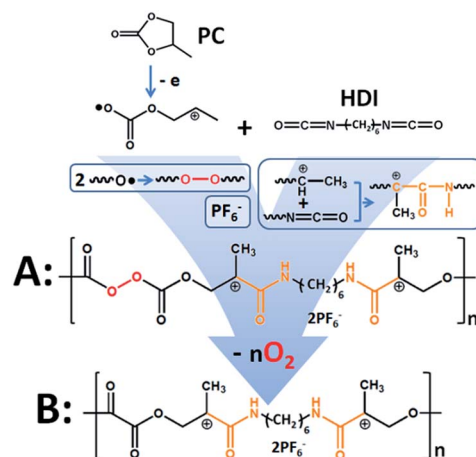


Fig. 2 XPS (left) and FTIR (right) spectra of the raw material and the surface of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode after 4.6 V(vs. Li/Li^+) – 3 h polarization in different electrolytes.

along the reaction processes as shown in Scheme 1. First, a PC molecule on the electrode surface should be electrochemically oxidized to a cation containing an oxygen free-radical and a positively charged methine at the ends of one onium ion.¹⁹ Free-radicals would dimerize to form peroxide groups, and the charged methines could react with isocyanate groups of HDI *via* nucleophilic addition to build amide groups.²⁰ Both addition reactions would form polymer A, in which the peroxide groups and amide groups are bridge-linked. Because the peroxide group is unstable, we conjecture that polymer A should be transferred to polymer B *via* decomposition–reaggregation.²¹ Since HDI does not form a protective layer with an EC-based electrolyte under the same conditions, we tend to attribute this difference to the absence of methyl protection,^{19b,22} which reduces the nucleophilicity of positive charge and lowers the reactivity with the isocyanate group.²³

The resistances of electrodes after 4.6 V(vs. Li/Li^+) – 3 h polarization are tested on a semiconductor parameter analyzer. Since the probe for the conductivity test is 50 nm, this measurement should reveal the variation of mono-particle's resistance. As shown in Fig. 3a, the tested value in the reference



Scheme 1 Schematic representation illustrating the formation of the surface layer *via* (i) decomposition of PC, (ii) radical polymerization and nucleophilic addition reaction, and (iii) decomposition–reaggregation.

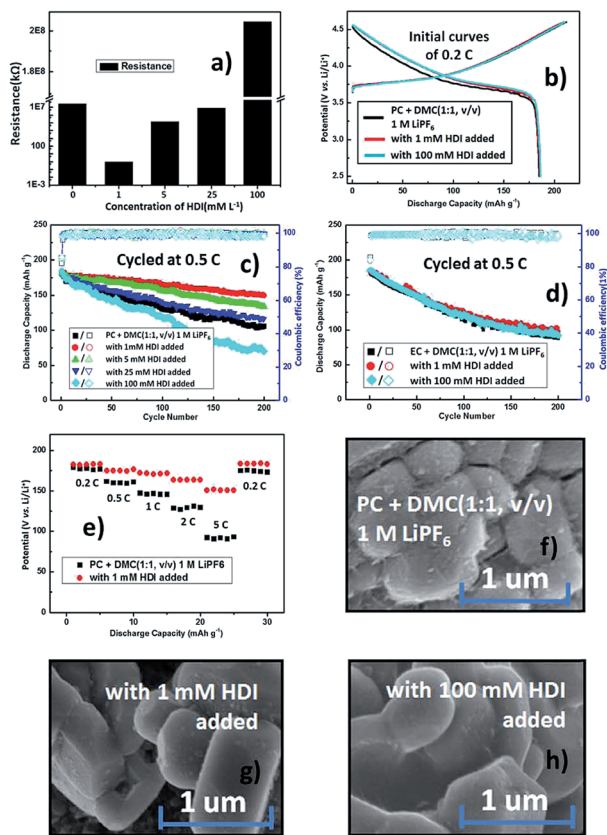


Fig. 3 The resistances of cathodes after being charged at 4.6 V(vs. Li/Li⁺) for 3 hours in different concentrations of HDI (a), comparison of the first charge–discharge curves at 0.2 C (b), effects of the additive concentrations on the cycling performance (c) in PC + DMC (1 : 1, v/v) 1 M LiPF₆ (c) and EC + DMC (1 : 1, v/v) 1 M LiPF₆ (d) between 2.5 and 4.6 V(vs. Li/Li⁺) at 0.5 C, comparison of the discharge capacity of electrolytes with and without 1 mM HDI from 0.2 to 5 C (e), and SEM images of cathodes after 200 cycles (f–h).

electrolyte is 2.8×10^7 kΩ, which is close to the range of single-particle LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.²⁴ After 1 mM HDI is added, the resistance surprisingly slumped by 7 orders to 1.0 kΩ. This significant improvement is probably rooted in the charged methine, in which electrons easily accumulate and transport quickly according to the quantum tunneling effect. With the increase of HDI concentration, the resistance is gradually enhanced to $\sim 10^8$ kΩ and even higher, indicating that the thick film would retard the kinetics of cathodes due to the improved polarization.

The influence of this protective layer on the electrochemical performance of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is evaluated in the coin cells with the electrolyte containing different HDI concentrations tested between 2.5 and 4.6 V(vs. Li/Li⁺). As shown in Fig. 3b, Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ delivers 183 mA h g⁻¹ in the reference electrolyte at 0.2 C. The first cycle charge–discharge curves for the electrolytes with HDI almost overlap with those of the control, indicating that the HDI additive does not play any function in the first cycle. Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ in the reference electrolyte seriously decays from 181 mA h g⁻¹ to 106 mA h g⁻¹ after the 200 cycle test at 0.5 C (Fig. 3c). In the electrolyte

containing 1 mM HDI, the discharge capacity at the 200th cycle is 149 mA h g⁻¹, 40.6% higher than that in the reference electrolyte. The capacity fading of the cells becomes serious with the increase of HDI concentration. The retained capacity at 100 mM is even lower than that of the reference system. This variation in cycling performance should be related to interfacial polarization, as shown in Tables S1, S2 and Fig. S3.† The cyclic curves are almost overlapped for the systems of the EC-based electrolytes with/without HDI (Fig. 3d). It further proves that HDI does not play a function in the system, which is consistent with TEM results as shown in Fig. 1.

Also the cell with 1 mM HDI presents improved rate capability. As shown in Fig. 3e, it still maintains 151 mA h g⁻¹ under 5 C, and 66.2% higher than the cell in the reference electrolyte. The surface morphologies after cycles are characterized by SEM images (Fig. 3f–h and S5†). Amorphous sediments are observed on the cathode in the reference electrolyte. In contrast, the surfaces of the cathode in the electrolyte with HDI are much smoother. Obviously, the film constructed from HDI could suppress the electrolyte decomposition at high potential. To some extent, the building of a surface layer would also suppress the particle cracking of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, as shown in Fig. 3f–h and S5.†

In summary, we have proved that HDI could build an efficient passivation layer to alleviate the side reaction between the electrolyte and cathode at high potential. This layer is generated from the direct chemical reaction of HDI and the onium ion produced by oxidative decomposition of propylene carbonate. The optimal system presents a similar discharge capacity at initial cycles, a better rate performance and a more stable rate-retention capability, when compared with the cells without HDI. Our results indicate that HDI could be used to construct a protective layer to widen the working window of practical batteries.

Acknowledgements

This work was supported by the 863 project (Grant no. 2013AA050906), the Zhejiang Key Innovation Team (Grant no. 2013PT16), the “Strategic Priority Research Program” of the Chinese Academy of Sciences (Grant no. XDA09010403), and the Hundred Talents Program of the Chinese Academy of Sciences.

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